

Advances in Studies of Electrode Kinetics and Mass Transport in AMTEC Cells

R. M. Williams, B. Jeffries-Nakamura, M. A. Ryan, M. L. Underwood, A. Kisor, D. O'Connor, and S. Kikkert

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

Previous work reported from JPL has included characterization of electrode kinetics and alkali atom transport from electrodes including Mo, W, WRh_x , $WPt_x(Mn)$, in sodium AMTEC cells and vapor exposure cells; and Mo in potassium vapor exposure cells. [Williams, *et al.*, 1990a, 1991, 1992] These studies were generally performed in cells with small area electrodes (about 1 to 5 cm²), and device geometry had little effect on transport. Alkali metal diffusion coefficients through these electrodes have been characterized, and approximate surface diffusion coefficients were derived in cases of activated transport. A basic model of electrode kinetics and transport at the alkali metal vapor/porous metal electrode/alkali beta"-alumina solid electrolyte (BASE) three phase boundary has been proposed which accounts for electrochemical reaction rates with a collision frequency near the three phase boundary and tunneling from the porous electrode partial] y covered with adsorbed alkali metal atoms. [Williams, *et al.*, 1990b, 1992]

The small electrode effect in AMTEC cells has been discussed in several papers, but quantitative investigations have described only the overall effect and the important contribution of electrolyte resistance. [Underwood, *et al.*, 1991] The quantitative characterization of transport losses in cells with large area electrodes has been limited to simulations of large area electrode effects, or characterization of transport losses from large area electrodes with significant longitudinal temperature gradients, [Weber, *et al.*, 1992] This paper describes new investigations of electrochemical kinetics and transport, with four 14.4 cm² WPt_3 electrodes, including the influence of electrode size on the mass transport loss in the AMTEC cell. These electrodes exhibit very slow sintering, as well as excellent sodium transport properties,

making them attractive candidates for AMTEC power conversion use. [Ryan, *et al.*, 1991, 1992] However, the facile sodium transport in WPt_3 electrodes makes characterization of the transport process difficult,

Experimental

Experiments used to evaluate electrode kinetics and transport were primarily carried out in the electrode test cell with multiple electrodes accessible separately through several electrical feedthroughs. The test cell has been modified to allow recirculation of sodium using two external reservoirs. Values of the dimensionless transport parameter, G , from recirculating cell tests were also used to evaluate electrode area and heat shield effects on transport. The thermal gradients in this cell were also thoroughly characterized using internal and external thermocouples on the Na-BASE tube and pyrometry utilizing two shutters and a small hole in the multifoil heat shield, [Ryan, *et al.*, 1993] WPt_3 electrodes were prepared by dc magnetron co-sputtering onto a rotating BASE tube substrate, and Mo mesh and bus wire current collectors were tied over the electrodes. The BASE tube brazed to a Nb tube contained heater and thermocouple wells and Na and vacuum connection tubes. AC impedance was the primary technique used for characterization of electrode kinetics and sodium vapor transport affecting the interracial sodium vapor pressure. The temperature dependence of kinetics and transport was evaluated by cycling the operating temperature. AC impedance was used to determine values of transport and kinetics parameters, at electrode temperatures from 884K and 1163K. AC impedance was evaluated following 420 hours of $T > 1000K$ operation. Morphology changes during

hours of operation during which the data were taken were minor, as were they during the remaining >1400 hours of the test, so that morphology changes with time did not convolute with the temperature dependence of these results significantly. Substantial morphology changes did occur during the first three hundred hours of the test, and the overall morphology studies are reported elsewhere.

Derived values of the collision normalized exchange current, B , and the dimensionless morphological parameter, G , vs. T , are shown in Fig. 1.

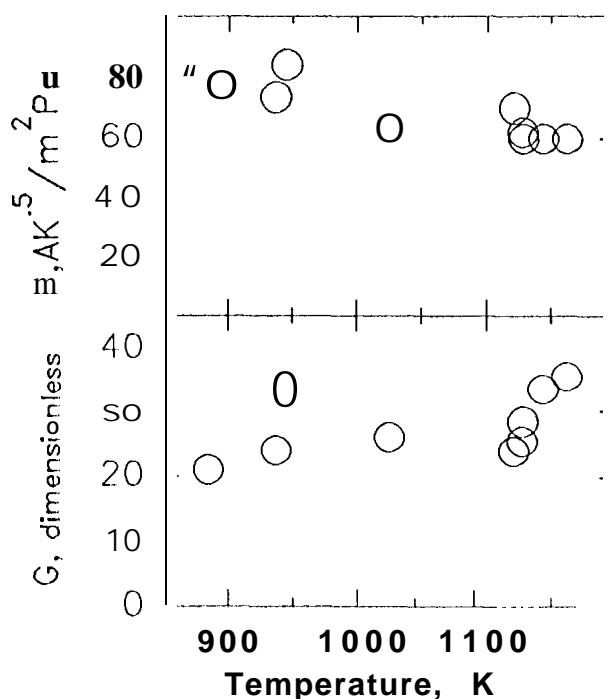


Fig 1. Electrode parameters B and G vs. $T(K)$ for WPt_3

The transport limitations were evaluated using four closely spaced 14.4 cm^2 electrodes at nearly constant temperature within a cylindrical multifoil heat shield at a distance of 0.75 cm from the electrodes on the surface of a $30 \times 1.5 \text{ cm}$ sodium beta"-alumina solid electrolyte (Na-BASE) tube; and characterizing the transport losses in single electrodes, all possible pairs and triplets of

electrodes, and all four electrodes operated simultaneously. $R_{act's}$, or Faradaic resistances, comprised of losses due to electrode kinetics and pressure gradients, were measured with ac impedance vs. potential, and the high potential portion of the data is shown in Fig. 2.

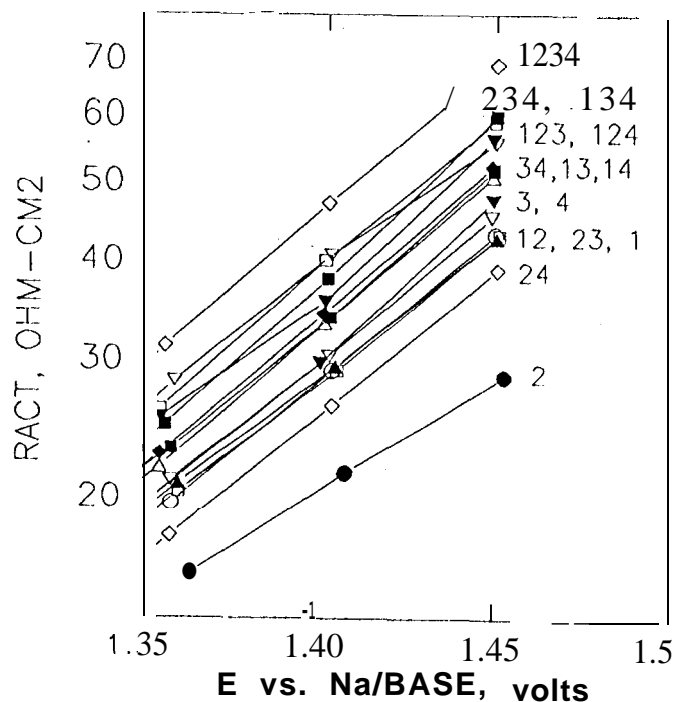


Figure 2. R_{act} vs. potential for sets of one to four electrodes

Results and Discussion

The thermal characterization, to be reported in detail elsewhere, made possible more precise evaluation of the temperature dependence of kinetics and transport in these electrodes from 884K to over 1162K.[Ryan, *et al*, 1993] Neither B nor G showed significant temperature dependence. The lack of strong dependence of B on temperature strongly supports the electrode kinetics model referenced earlier. However, surface or grain boundary sodium transport was expected and is supported by the low values of G for low porosity electrodes. The best performing electrode, E#2, with values of G about half those of E#3, was significantly less porous than E#3. As discussed below, pressure drops due to the heat shield contribute significantly to the low values of G , and

it is possible that the transport mode within the electrode was too rapid throughout the temperature range to evaluate. The area averaged Faradaic loss increased substantially with number of electrodes operated in parallel. Although electrodes E# 1 and E#4 were somewhat cooler than E#2 and E#3, by averaging the Faradaic impedances of all electrodes and groups of electrodes in order to calculate values of a transport parameter at the average electrode temperature, 111 SK, designated G' , a plot of the effect of electrode area on transport could be constructed. All electrodes contributed equally to each value of G'_{ave} , so that although G' values each have a small systematic error, the dependence of G'_{ave} on area has no systematic contribution from this error. Fig. 3 shows a plot of G'_{ave} vs. total electrode area,

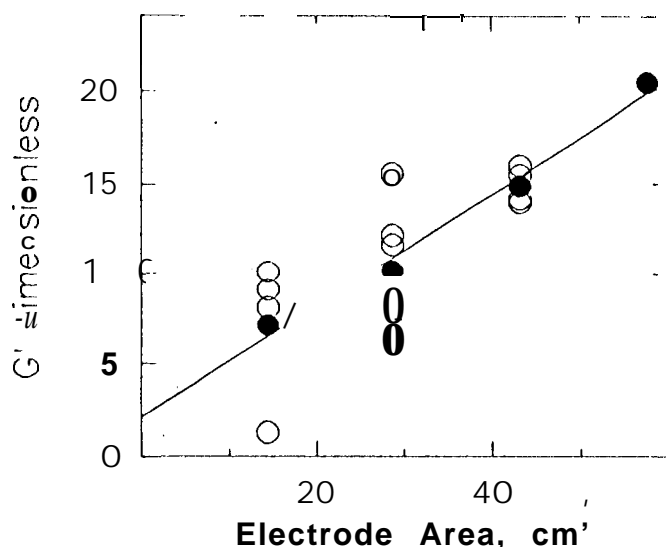


Fig. 3 Transport parameter vs. area
Average value solid circle

"Edge" effects on transport are fairly negligible on all electrode areas in this area range, so the zero area intercept indicates, for the most part, not the transport parameter of a point or line electrode dominated by "edge" effects, but rather the transport behavior of an electrode area element unaffected by backpressure from a heat shield due to adjacent electrode area elements. As Fig. 3 shows, the zero area intercept gives a small G' value, but G' values were generally smaller than values of G for single electrodes. The slope does show a significant area dependence, and effects of

averaging the electrodes temperature weigh equally on each average G' . G for single electrodes was generally in the range of **20 to 80**, for other impedance measurements run on this cell's electrodes. Measurements of G in a recirculating test cell with a closer (about 0.5 cm) heat shield gave values of at least 200, for a 100 cm² electrode WPt_{2,5} electrode, showing the magnitude of the effect on transport of a heat shield or, equivalently, a remote condensed cylindrical design,

Conclusions

WPt₃ electrodes are possibly the best candidate electrodes for AMTEC modules for moderate length planetary exploration missions where wide temperature range performance is required. The collision normalized exchange current of these electrodes has little or no temperature dependence, in strong agreement with the model previously proposed which depends on tunneling from an alkali metal coated porous metal electrode, with a low work function, to nearby BASE surface confined Na⁺, at the very long three-phase interface. Transport in these electrodes is very good, but vapor-phase transport can not account for it, nor can rate parameters for an surface confined mode be determined, due to the high rate.

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References

- Ryan, M. A.; Jeffries-Nakanmra, B.; Williams, R. M.; Underwood, M. L.; O'Connor, D.; Kikkert, S.; in *Proc. 27th IECEC*; Bland, T., Ed., SAE, Warrendale, PA, 1992, Vol. 3, 7.
- Ryan, M. A.; Kisor, A.; Williams, R. M.; Jeffries-Nakamura, B.; Underwood, M. L.; O'Connor, D.; in *Proc. 28th IECEC*; (this volume) ACS, 1993

Ryan, M. A.; Jeffries-Nakamura, B.; O'Connor, D.; Underwood, M. L.; Williams, R. M.; *Proc. Sym. on High Temp. Electrode Mat. Char.*, Macdonald, D. D.; Khandkar, A. C.; eds., The Electrochem. Soc., Proc. 1991, Vol. 91-6, 115.

Underwood, M. L.; Williams, R. M.; Hunt, T. K.; Schmatz, D. J.; *Electrochem. Soc. Ext. Abstr.*, The Electrochemical Society 1991, 91-1, 1.

Weber, N.; Rasmussen, J. R.; Olsen, S. L.; in *Proc. 27th IECEC*, Bland, T., Ed., SAE, Warrendale, PA, 1992, Vol. 3, 117.

Williams, R. M.; Jeffries-Nakamura, B.; Ryan, M. A.; Underwood, M. L.; O'Connor, D.; Kikkert, S.; in *Proc. 27th IECEC*, Bland, T., Ed., SAE, Warrendale, PA, 1992, Vol. 3, 19.

Williams, R.; Jeffries-Nakamura, B.; Underwood, M.; Ryan, M. A.; O'Connor, D.; Kikkert, S.; *Proc. Sym. on High Temp. Electrode Mat. Char.*, Macdonald, D. D.; Khandkar, A. C.; eds., The Electrochem. Soc., Proc. 1991, Vol. 91-6, 103.

Williams, R. M.; Loveland, M. E.; Jeffries-Nakamura, B.; Underwood, M. L.; Bankston, C. P.; Leduc, H.; Kummer, J. T.; *J. Electrochem. Soc.*, **1990a**, **137**, **1709**.

Williams, R. M.; Jeffries-Nakamura, B.; Underwood, M. L.; Bankston, C. P.; Kummer, J. T.; *J. Electrochem Soc.*, **1990b**, **137**, **1716**.